Interaction of Carbon Dioxide With Hydrogen Chemisorbed on a Platinum Electrode

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CONTENTS

ABSTRACT

The effect of CO_2 on the oxidation of H atoms chemisorbed on a Pt electrode is examined with potentiostatic and transient galvanostatic techniques. The results indicate that CO_2 is not reduced, but that H_{ad} oxidation is inhibited by CO_2, or possibly HCO_3^-. Under these conditions the inhibited or blocked H_{ad} is stable at potentials negative to 0.300 V (vs N.H.E.). Dissociation of HCOOH to H_{ad} and CO_2 may inhibit the further oxidation of HCOOH by a similar blocking mechanism.

PROBLEM STATUS

AUTHORIZATION

INTERACTION OF CARBON DIOXIDE WITH HYDROGEN
CHEMISORBED ON A PLATINUM ELECTRODE

INTRODUCTION

Fuel cell research in recent years has shown that under proper conditions a large variety of organic compounds can be oxidized to produce electrical power. Organic systems used at present, however, give relatively low half-cell potentials, have high overvoltages, and show effects of poisoning after short use times. In general, the open-circuit half-cell potentials of organic reactants at a Pt electrode are remarkably similar. This and also the similarities in overvoltage and self-poisoning behavior have led us to suspect that a common cause exists. Our feeling was that organic reactions could generate a common species that affected the subsequent oxidation of these compounds.

Our approach to the study of mechanisms of organic oxidation reactions has been to determine the reason for their common behavior and to determine why organic fuels so far have failed to deliver the power and operate at the efficiencies that would be necessary for successful fuel cell application. Our initial endeavor in this direction was to study the electrochemistry of the oxidation of CO on Pt (1). This was followed by an investigation of the displacement of adsorbed H atoms with CO molecules (2). These investigations showed that even very small traces of CO would have undesirable effects on the anodic polarization of organic fuels.

The object of any successful electrochemical oxidation of an organic fuel is to completely oxidize all C to CO_2 and all H to H_2O. It is well known from catalytic studies that H-containing organic compounds often dissociate at a Pt surface to give H atoms that are chemisorbed. Thus at any Pt surface where an anodic organic reaction occurs, there is a strong possibility that chemisorbed H atoms (H_{ad}) and CO_2 will coexist. We have felt that the interaction of H_{ad} with CO_2 may give a clue concerning the common electro-chemical behavior of many organic reactants.

The interaction of CO_2 with electrolytically generated hydrogen at Pt electrodes in acid solution has been reported by Giner (3), who demonstrated a difference between the anodic polarization behaviors of hydrogen-covered electrodes in saturated solutions of CO_2 and He. Giner concluded that CO_2 is reduced by reaction with H_{ad} between 0.000 and 0.250 V (all potentials are versus the N.H.E.). The chemisorbed product, which he called reduced CO_2, was oxidized at about 0.700 V, 25°C, during anodic galvanostatic polarization and from 0.500 to 0.900 V during linear potential sweeps.

This study was designed to demonstrate that the experimental results observed by Giner were indeed due to his assumed interaction (or reaction) and not to an oxidizable impurity, to investigate the nature of the adsorbed oxidizable species, and to examine the implications of such an interaction on the interpretation of anodic organic reactions.

EXPERIMENTAL METHOD

Apparatus

The electrolytic cell (Pd tube and miniature glass reference electrodes, large Pt gauze counter electrode, and 0.19 cm^2 true area Pt bead working electrode), purification

of He and H_2, and general procedures were as previously described (4,5). High-current galvanostatic pulses (2.33 A/cm^2) were obtained with an Electro-Pulse Model 3450D generator. Low constant currents were applied either from an Electronic Measurements Company C-612 constant current supply (0.2 mA/cm^2 to 0.6 μA/cm^2) or a Keithley Model 600A electrometer (down to 0.05 μA/cm^2), both being switched manually. Cell polarization was either observed and photographed on a recalibrated Tektronix Type 547 oscilloscope or recorded on a Varian Associates Model G-11A strip chart recorder from the output of a Keithley Model 603 electrometer amplifier. Constant potentials were maintained with a Wenking Model 61-R fast-rise potentiostat. All current densities are expressed in terms of true area, as determined from the charge required to deposit one monolayer of O atoms.*

Baker Analyzed Reagent Grade CO_2 (99.9992% purity; 1.5 ppm O_2; 6 ppm N_2 + CO) was purified by passage through a trap containing, at different times, Pd catalyst supported on alumina at -50°C, palladium oxide supported on alumina at 400°C, or Hopcalite followed by Cu turnings to remove traces of O_2 generated by the Hopcalite, both held at 350°C.

Galvanostatic Technique

Anodic charging curves were obtained in 1M H_2SO_4 solutions saturated at 25°C with purified He, CO_2, or a mixture of 22% H_2 and 78% CO_2. The dependence of the charging curves on potential and time was examined. Before taking each charging curve, the electrode was either left at open circuit until the potential became stable or potentiostated at a given potential. The open-circuit potentials were always 0.300 V or less, indicating a low concentration of oxygen in the electrolyte as a result of gas purification, tightness of the closed system, and oxygen gettering by the Pd-tube reference electrode (which contained enough dissolved hydrogen to maintain a stable αPd-H potential of +0.055V). The working electrode was always anodized in such a way that dermasorbed oxygen, namely, oxygen dissolved into the skin of the Pt (4,6), would not be formed. Since experiments showed that the results were independent of the gas flow rate, a convenient rate was established and the chosen sequence of currents and/or potentials was applied.

In the low-current experiments, the fixed current was switched from anodic to cathodic values before a significant amount of oxygen could be generated. In the high current experiments the electrode was cleaned with a 2.33-A/cm^2 anodic pulse, which was limited to less than 500 μsec to avoid formation of dermasorbed oxygen. Immediately following the cleaning pulse, the electrode potential was fixed with the potentiostat for a given time to allow interaction of CO_2 and H_{ad}. This was followed by another 2.33-A/cm^2 anodic pulse, applied to determine the amounts of sorbed H, H_{ad}-CO_2 (H_{ad}-CO_2 merely signifies the presence of both species on the surface), and O_{ad}. Manual switching between galvanostatic and potentiostatic control was used, with switching times being less than 0.5 sec. The time of switching was not important, since it was established that the amount of H_{ad}-CO_2 formed at a given potential in a set interaction time was unchanged at open circuit for at least 72 hours. The first pulse (or cleaning pulse) rapidly anodized the electrode to O_2 evolution, removed previously sorbed H_{ad}-CO_2, and provided a reproducible state. Thus, just prior to potentiostatic control, the electrode was free from dermasorbed oxygen and H_{ad}-CO_2. Each successive pulse not only gave the required charging curve, but stripped the surface of H_{ad}-CO_2 and presented a clean surface for the start of another experiment. The current pulses for a given current density were of equal duration.

*The electrode area remained unchanged after 45 days of continuous use, which included extended periods of anodization during pre-electrolysis. The constancy of areas of the bright Pt beads is a general observation in this Laboratory. Barring failure in the mounting, an electrode area change has never been observed during normal use over periods as long as 6 months.

Fig. 1 – Oscillograms of anodic charging curves in $1M$ H_2SO_4 at $25°C$, with a current of 0.2 mA/cm^2. (a) He flow rate is 88 std cc/min. Trace 1 begins at the open-circuit potential of 0.065 V, and trace 2 immediately after a 10-sec cathodization to deposit chemisorbed H. In each case, the current was reversed at 0.8 V to prevent deposition of oxygen. (b) CO_2 flow rate is 4 std cc/min. Trace 1 begins at the precathodized potential of 0.000 V, and trace 2 follows trace 1 after a stable open-circuit potential of 0.050 V was attained. The new region that appears at 0.690 V is characteristic of the CO_2-inhibited H_{ad}.
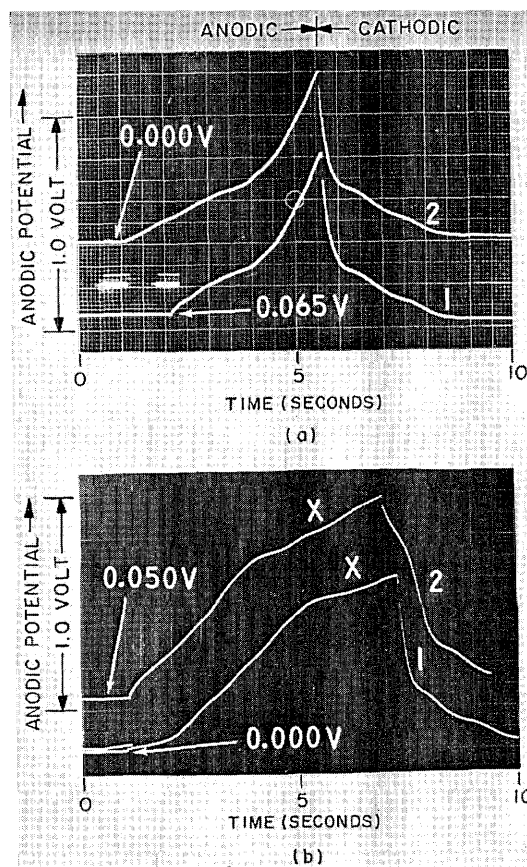
RESULTS

Low Current Galvanostatic Charging Curves

After the cleanliness of the electrolyte and electrode surface had been established,* charging curves were obtained with He at a flow rate of 88 std cc/min (Fig. 1a) and then with CO_2 at a flow rate of 4 std cc/min† (Fig. 1b). In trace 1 of Fig. 1a, the electrode was anodized from the open-circuit potential of 0.065 V to 0.800 V and then cathodized to 0.000 V. In trace 2, this procedure was preceded by 10-sec cathodization to deposit chemisorbed H. In each case, the current was reversed at 0.800 V, avoiding the deposition of oxygen as verified by the absence of linear O-atom adsorption regions in the charging curves.

Analysis of these charging curves in He-saturated solution shows that the anodic charge in $coul/cm^2$ required to polarize the electrode to 0.800 V (Q_a) increases as stirring rate decreases, as the potential from which charging was started decreases, and as the time of precathodization increases. These observations are attributed to oxidation of the hydrogen generated during precathodization that would contribute to Q_a. In solutions stirred with He flowed at 88 std cc/min, Q_a varied from 600 $\mu coul/cm^2$ when anodization was begun at the open circuit potential of 0.065 V, to about 900 $\mu coul/cm^2$ for 10-sec precathodization, to about 1000 $\mu coul/cm^2$ for 40-sec precathodization. The cathodic charge in $coul/cm^2$ required to polarize the electrode from 0.800 V to 0.000 V

*The linearity of voltage vs time in the O-atom adsorption region has been found to be a reliable test of electrode cleanliness (7). Typical linear regions are seen in Fig. 3.
†Varying the flow rates of CO_2 from 4 to 250 std cc/min did not affect the charging curves.

(Q_c) remained roughly constant at 520 ± 40 $\mu coul/cm^2$. The variation between Q_a and Q_c noted here differs from Giner's results, in which he found the anodic and cathodic branches roughly equal.

Figure 1b is typical of the charging curves obtained when CO_2 was substituted for He. Trace 1 was taken after 10-sec precathodization and trace 2 was taken from the open-circuit potential of 0.050 V. The new plateau that appears at 0.690 V (designated region X by Giner) was well below the potential of O-atom formation. Region X developed slowly, requiring about 15 min at open circuit to reach a maximum. Q_a was independent of the stirring rate with CO_2, indicating that the electrode surface had become passive to the oxidation of hydrogen formed in precathodization.

Purification of CO_2

Slow adsorption of traces of an oxidizable impurity could affect both the appearance of the charging curves and the time required for the X region to develop. CO is one trace impurity possibly present in the CO_2 used, and previous work (1, 7) has shown that extremely small amounts of CO will affect charging curves. Accordingly, the purification techniques used were designed either to remove trace amounts of CO and organic compounds or to oxidize them completely to CO_2. Since it is difficult to prove the absence of impurities, the criterion for acceptably pure CO_2 was that the X region should develop identically after the CO_2 was purified in several ways in separate experiments, namely, by passage through Pd at -50°C, palladium oxide at 400°C, and Hopcalite and Cu at 350°C. The strong chemisorption of CO on Pd is well known (8), thus a Pd cold trap should be highly specific for CO and also very efficient for most organic impurities. Palladium oxide and Hopcalite were used to oxidize any organic impurities present completely to CO_2. In every experiment, the X region developed identically.

CO_2 was replaced with He between each set of experiments and the electrode was tested for cleanliness. Figure 2 presents typical results, in this case obtained 65 min after starting the flow of He. Trace 1 shows that H_{ad}-CO_2 is adsorbed strongly enough to give the equivalent of a full monolayer, assuming a one-electron discharge. Further experiments showed that even after 75 hours of He flow, a full monolayer was still present on the electrode. After the electrode surface was cleaned by the first pulse, trace 2 shows that no oxidizable material is adsorbed from solution.

Finally, to eliminate the possibility of slow adsorption of solution impurities, charging curves were taken after a waiting period at open circuit. Trace 2 of Fig. 3, in which figure there was a period of 13 min between pulses, shows no evidence of adsorption of oxidizable impurities.

High Current Galvanostatic Charging Curves

The rate of formation of H_{ad}-CO_2 was examined as a function of both potential and interaction time. Figure 4 shows the amount of Q_X in certain time intervals when various electrode potentials are employed.

Figure 5 presents typical results of the influence of interaction time on the amount of H_{ad}-CO_2 formed at a given potential, in this case 0.000 V. As the interaction time increases, a dip, characteristic of the oxidation of many organic compounds, develops in the O region at approximately 0.9 V in the case of high-current pulses. Paralleling this oxidation plateau is the decrease in length of the usual H region.

The following quantities were determined from the oscillograms, in terms of $\mu coul/cm^2$: (a) Q_t, the total charge required to polarize the electrode to the potential at which

Fig. 2 - Oscillograms of charging curves in $1M\,H_2SO_4$ at $25^\circ C$, with a current of 0.2 mA/ cm^2 and a He flow rate of 56 std cc/min. These traces show the irreversibility of CO_2 adsorption. Results were obtained 65 min after starting He flow. Trace 1 was taken from the open-circuit potential of 0.050 V and shows that the poisoning effect of CO_2 or HCO_3^- is still present after all the CO_2 has been removed. Trace 2 was taken after a 10-sec precathodization, and is characteristic of a clean surface.
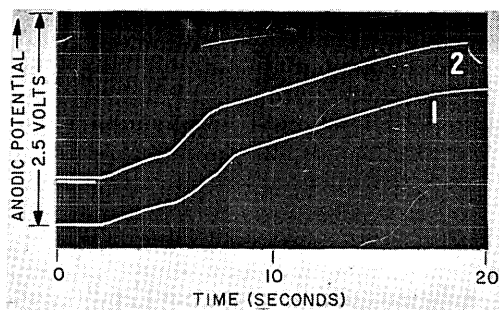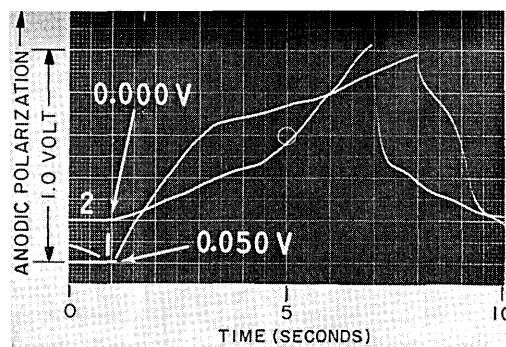

Fig. 3 - Oscillograms of charging curves in $1M\,H_2SO_4$ at $25^\circ C$, with a current of 0.2 mA/ cm^2 and a He flow of 56 std cc/min. The traces were taken after a waiting period at open circuit to test for electrode cleanliness. Neither shows any evidence of adsorption of oxidizable impurities. Trace 1 was taken 2 min after the preceding polarization and after a 60-sec precathodization. Trace 2 was taken 13 min after the preceding polarization and after a 10-sec precathodization period.
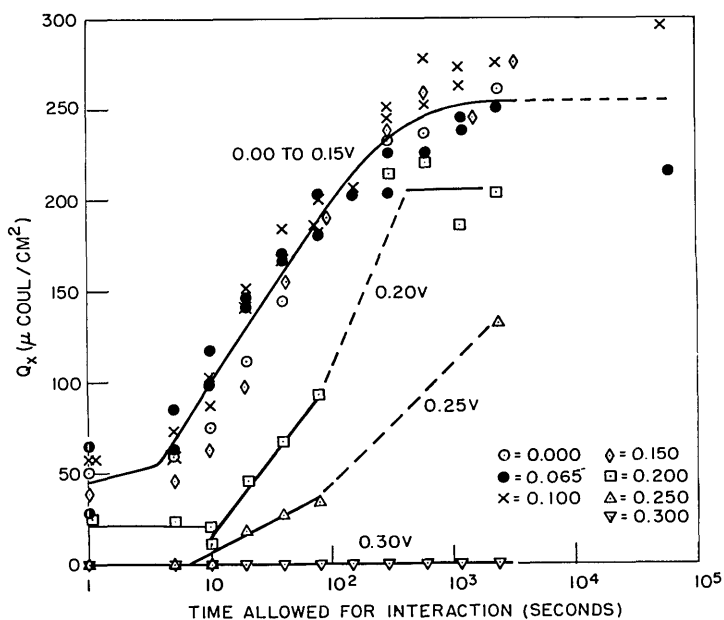

Fig. 4 - Amount of Q_x as a function of time; electrodes were held at different potentials during interaction time
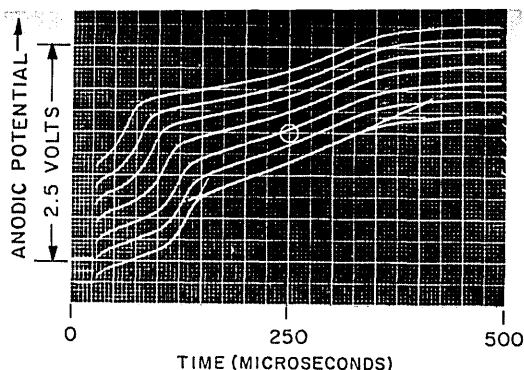
Fig. 5 - Oscillograms of charging curves in $1M\ H_2SO_4$ at 25°C, with a current of 2.33A/cm² and a CO_2 flow rate of 2 std cc/min. Electrode potential was held at 0.000 V between pulses. The effect of time on the X region is shown. The lowest pulse was taken 1 sec after the initial pulse, and succeeding pulses reading upward were taken 5, 10, 20, 40, 80, and 300 sec after the preceding pulse. Note the dip occurring in the O region at about 0.900 V for longer interaction times, and also note the gradual decrease in the length of the normal H region.

O_2 evolution occurs; (b) $(Q_H + Q_{Hdl})$, the quantity of charge required to polarize the electrode to the potential at the start of the X region (H atom oxidation and double layer charging); and (c) $(Q_O + Q_{Odl})$, the quantity of charge required to polarize the electrode from the start of the X region to the potential of O_2 evolution (oxidation of adsorbed species, formation of a monolayer of O atoms and double-layer charging). Thus,

$$Q_t = Q_H + Q_{Hdl} + Q_O + Q_{Odl}. \tag{1}$$

For a clean Pt electrode (3) in the absence of CO_2,

$$Q_O^{CO_2\text{-free}} + Q_{Odl}^{CO_2\text{-free}} = 426\ \mu coul/cm^2 + 36\ \mu coul/cm^2$$

$$= 460 \pm 20\ \mu coul/cm^2. \tag{2}$$

Assuming the charge required to form one monolayer of O atoms and to charge the double layer is identical for saturated solutions of CO_2 and He, then

$$Q_X = Q_O + Q_{Odl} - 460\ \mu coul/cm^2, \tag{3}$$

where Q_X is the charge required to oxidize H_{ad}-CO_2.

When the electrode was potentiostated at 0.000 V, Q_t reached a limiting value in less than 1 sec and remained constant as the interaction time increased; that is, as Q_H decreased, Q_O increased by an equivalent amount. As the electrode was held at successively more positive potentials, longer interaction times (which, however, were always less than 2400 sec) were required to reach a limiting value of Q_t. These data are collected in the second and third columns of Table 1. For comparison, the values of $Q_t^{CO_2\text{-free}}$ (Q_t in CO_2-free solution) are given in the fourth column. $Q_t^{CO_2\text{-free}}$ values were determined by adding $\left(Q_O^{CO_2\text{-free}} + Q_{Odl}^{CO_2\text{-free}}\right)$, given above, and $Q_H^{CO_2\text{-free}}$ $+Q_{Hdl}^{CO_2\text{-free}}$, derived from data obtained previously for H coverage of Pt electrodes as a function of open-circuit potential and for double-layer capacity as a function of potential (Figs. 10, and 5, in Ref. 5). The comparison in the fifth column of $Q_t^{CO_2\text{-free}}$, obtained in this way, with Q_t implicitly assumes that the coverage of a Pt electrode by H is the same when the electrode is at a given potential at open circuit and when it is maintained at this potential with a potentiostat. Limiting Q_X values, as determined using Eq. (3), are given in the sixth column. Limiting Q_H values, obtained from the anodic charging curves and corrected for double-layer charging, are found in the seventh column.

Table 1*
Coulometric Data Obtained From High-Current Charging Curves

Electrode Interaction Potential (V)	Q_t Observed After 1 sec Interaction (μcoul/cm^2)	Q_t Observed Limiting Value (μcoul/cm^2)	Q_t CO_2-free (μcoul/cm^2)	$Q_t - Q_t$ CO_2-free Limiting Value (μcoul/cm^2)	Q_x Limiting Value (μcoul/cm^2)	Q_H Limiting Value (μcoul/cm^2)
0.300	489 ± 25	478 ± 25	487 ± 25	0 ± 35	0 ± 35	0 ± 25
0.250	512 ± 25	652 ± 25	518 ± 25	134 ± 35	132 ± 35	0 ± 25
0.200	594 ± 25	700 ± 25	552 ± 25	148 ± 35	202 ± 35	0 ± 25
0.150	629 ± 25	746 ± 25	586 ± 25	160 ± 35	274 ± 35	0 ± 25
0.100	652 ± 25	769 ± 25	638 ± 25	131 ± 35	285 ± 35	0 ± 25
0.065	769 ± 25	775 ± 25	669 ± 25	106 ± 35	231 ± 35	30 ± 25
0.000	785 ± 25	789 ± 25	729 ± 25	60 ± 35	260 ± 35	50 ± 25

*For explanation of symbols, see text.
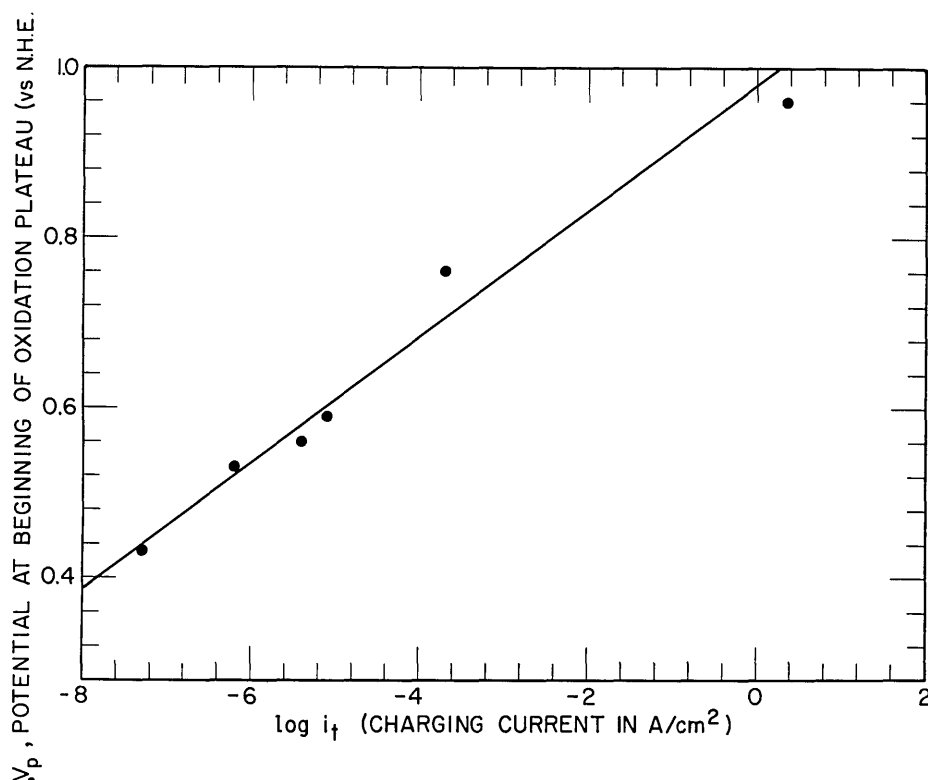
Fig. 6 – Dependence of the potential at the beginning of the oxidation plateau V_p, on the applied anodic charging current density, i_t. Note that V_p is directly proportional to the logarithm of i_t.

The potential, at which oxidation of H_{ad}-CO_2 first occurs, V_p, is directly proportional to the logarithm of the current density. Measurements of V_p, that is, the potential at the beginning of the X region, were made on charging curves obtained at different charging currents (Fig. 6).

DISCUSSION

This work shows that the actual reduction of CO_2 by H_{ad} is neither a necessary or likely explanation of the interaction between the two. Limiting Q_X values found at interaction potentials below 0.250 volt (see Table I) show that the "X-region" is virtually saturated with an oxidizable species. On the other hand, V_p was found to depend only on charging current (Fig. 6). If a reduced CO_2 surface compound were formed, then V_p should depend on current density only if the oxidation rate depended on a slow charge transfer or chemical reaction step following charge transfer. However, if the oxidation were dependent on a charge transfer or chemical rate, then the degree of surface coverage of the reduced CO_2 should affect the initial oxidation potential. The results, as shown, e.g., in Fig. 5, indicate that V_p is independent of the degree of coverage, strongly suggesting that no reduced CO_2 species is oxidized, i.e., that CO_2 is not reduced. Further evidence against the possibility of CO_2 reduction is seen in Fig. 4 which shows that Q_X is independent of the interaction potential and hence H_{ad} concentration from 0.00 to 0.15 V.

The experimental results can be explained if there exists on the electrode surface only a small number of active sites at which oxidation can occur (e.g., most of the sites could be blocked for oxidation by another species) and the process involves diffusion of the oxidizable species to these sites. It is well known that there are several types of sorbed atomic H. If the concentration of active H_{ad} were low, the rate of oxidation could be affected by the rate of diffusion of irreversibly held H atoms. At low current densities diffusion of H atoms to reactive sites would be fast enough to maintain a relatively constant coverage of these sites. At high current densities a diffusion overvoltage of H atoms would increase V_p. This mechanism is supported by the fact that V_p is independent of Q_X whereas in the "X region," the potential increases as the H coverage decreases. As a further check, an intensive search to detect traces of a reduced CO_2 compound in solution, was made using charging curves after long periods at open circuit (Fig. 2), and none were ever found. In addition, Johnson and Kuhn (9) were unable by chemical analysis to detect a reduced CO_2 compound in solution, after 24 hours of reaction.

There is concrete evidence that CO is not formed. CO oxidation begins in the potential range of 0.900 to 1.300 V, depending on the CO partial pressure (1). The oxidation potential caused by the H_{ad}-CO_2 interaction depends on the charging current (Fig. 6), but in every case is below 1.00 V. Under potentiostatic conditions, the equivalent of a full monolayer of H_{ad} can be rapidly removed (0.5 sec) at 0.300 V, while from published (1) and unpublished work at this Laboratory CO appears to be unreactive to 0.900 V under both transient and steady-state polarizations. Even at low coverages, a typical CO oxidation plateau at about 0.900 V is observed with CO in solution. When much less than a monolayer of CO is allowed to adsorb on a Pt electrode that has been precathodized to evolve H_2, a characteristic H arrest at about 0.550 V can be observed, in addition to the small CO plateau (Fig. 2b in Ref. 2). This arrest is due to the oxidation of tightly bound H atoms that have not been displaced. At somewhat higher coverages of CO, no evidence of any arrest below 1 V was found (Fig. 2a in Ref. 2). Furthermore, the shapes of the anodic charging curves for the X region are markedly different from those for CO oxidation, both in the presence and absence of hydrogen (1,2).

Analysis of the data in Table 1 and Fig. 4 shows that when high-current anodic charging pulses are used:

1. At a given potential, more hydrogen is generated on the electrode when CO_2 is present than is formed in CO_2-free solution (column 5 in Table 1).

2. At sufficiently long interaction times (which were dependent on the potential but less than 2400 sec), most of the H-ionization region - normally associated with a Pt electrode in CO_2-free solution at a given potential disappears (column 7 in Table 1). Small H

regions were found at 0.000 and 0.065 V, indicating that some active H_{ad} remains at these potentials.

3. Q_X is constant at about 260 ± 35 $\mu coul/cm^2$ for potentials negative to 0.200 V (column 6). Assuming a one-electron reaction, this charge is approximately equal to the 230 $\mu coul/cm^2$ required to oxidize the H normally adsorbed on a clean Pt electrode at 0.000 V. This suggests that in the presence of CO_2 essentially a full monolayer of H atoms is generated up to 0.200 V, but that above this potential not enough H is produced to form a monolayer.

The most probable effect of CO_2 on H_{ad} is one which shifts the equilibrium of the reaction

$$H_{ad} = H^+ + e^-,\qquad (4)$$

so that at a given interaction potential the formation of additional H_{ad} is favored. Giner previously inferred a similar shift in equilibrium. The data of column 5 shows that $Q_t - Q_t^{CO_2-free}$, the equivalent excess found after H_{ad}-CO_2 interaction over the amount of H_{ad} found in CO_2-free solutions, is essentially independent of potential between 0.100 and 0.250 V. The total amount of Q_X(column 6), which includes the equivalent of H normally present under CO_2-free conditions plus the excess H found in the presence of CO_2, decreases rapidly between 0.150 and 0.200 V, however. It is thus inferred that the excess H required to give the values indicated in column 5 is all strongly bonded to Pt, since active H, that is, reversibly held H, will not be formed at these more positive potentials.[*] In other words, since reversibly held H atoms apparently cannot exist about 0.150 V, only H atoms strongly bound or alloyed to Pt can be formed, and since the sites available for these atoms will be limited, the equivalent of a full monolayer of CO_2-blocked H_{ad} cannot build up.

Fig. 7 - Cathodic steady-state current density vs potential in vigorously stirred solutions (current density is independent of higher gas flow rates). ●Schuldiner (18); ■ solution stirred with helium at 690 std cc/min; ▲ solution stirred with a CO_2-He mixture at rates >690 std cc/min. At a given potential, the current density for the CO_2-He mixture is always less than that for the pure He.
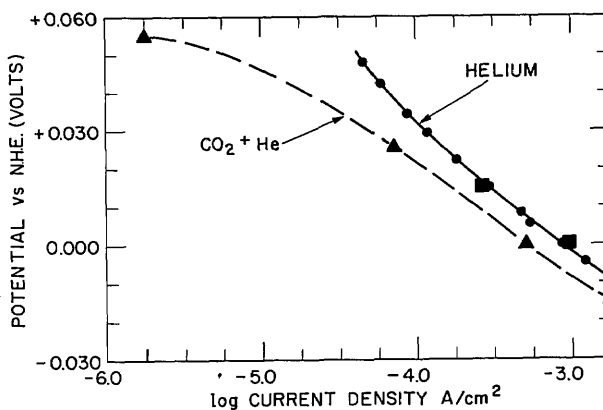
The fact that CO_2 can inhibit H_{ad} reactions on a Pt electrode is confirmed in Fig. 7, which compares the cathodic polarization behaviors in 1M H_2SO_4 saturated with a CO_2-He mixture and with pure He. Behavior in pure CO_2 was found to be essentially the same

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[*]Recent work in this Laboratory has shown that the Nernst potential relation for an H^+/H_2 electrode on Pt in a system in which O_2 leakage is so low that the equivalent O_2 partial pressure above the solution is less than 10^{-9} atm holds only to 0.180 V (10^{-6} atm H_2). This 0.180-V potential is independent of the H_2 partial pressure below 10^{-6} atm. Hence, at potentials of 0.180 V and higher, the H^+/H^2 exchange is not potential determining and the intermediate H_{ad} activity must be negligibly small. The conclusion that reversibly held H atoms cannot exist above about 0.180 V thus appears valid.

as in the CO_2-He mixture. He was added to increase gas stirring rates to establish a limit beyond which increased stirring did not increase current density. At a given potential, the current density for the CO_2-He mixture is always less than that for the pure He.

It is difficult to see how CO_2 itself could act as an electrode poison. One possibility is that the HCO_3^- or $CO_3^=$ ions present in solution are the poisons. The formation of complexes having HCO_3^- or $CO_3^=$ structures in the gas-phase adsorption of CO_2 has recently been suggested (10). The poisoning effects of these anions could then be similar to the effects of I^- on the rate of H ionization in H_2SO_4, reported by Shanina (11), who found the poisoning effect to occur slowly. Slygin and Frumkin (12,13) showed that the shapes of anodic charging curves for H ionization depend on the anion in solution. For example, several plateaus that were present for oxidation in H_2SO_4 could not be detected in HCl or HBr. From arrests in the charging curves on platinized Pt in H_2SO_4 at about 0.700 V, Slygin and Frumkin suggested that some H could be so firmly bound as to require this higher potential for oxidation. The fact that they obtained a lengthening of this plateau with more intensive platinization, which presumably generated more sites at which H atoms could be strongly adsorbed, argues against solution poisoning. Their results do suggest that under certain conditions a much higher potential than expected is required to oxidize H.

Although the concentration of $CO_3^=$ will be vanishingly small in 1M H_2SO_4 at 1 atm CO_2, HCO_3^- will be present in solution at approximately 10^{-8} M (14), and could be at a somewhat higher concentration in the double layer. Anions present at 10^{-8} M could easily poison a Pt electrode, but this would depend on the reversibility of adsorption. In the absence of any detailed knowledge of the adsorption of HCO_3^- on Pt, this suggestion must remain open to question. Teeter and Van Rysselberghe (15) found that while CO_2 was reduced to HCOOH with virtually 100% current efficiency, HCO_3^- was electrochemically inactive. However, it should be mentioned that their reaction was at high negative potentials where anion adsorption would be expected to be negligible. Since CO_2 inhibits H_{ad} on the Pt surface at low cathodic potentials,* this eliminates the possibility that HCO_3^- might be the poisoning species at anodic potentials but be desorbed when the Pt surface is negatively charged.

Giner (16) concluded that upon anodic oxidation on Pt, and to some extent at open circuit, CH_3OH and HCOOH gave a product which was the same as that formed by reaction of CO_2 with H atoms. He considered that the CO_2 was reduced by H atoms. We believe that in HCOOH solution dissociation to H_{ad} and CO_2 takes place and that inhibition of H_{ad} or HCOOH oxidation results. This interaction of the products of dissociative adsorption has several implications for the anodic oxidation of organic compounds, and particularly for HCOOH. The dissociative mechanism for HCOOH oxidation,

$$HCOOH \quad = \quad HCOOH_{ad} \tag{5}$$

$$HCOOH_{ad} = H_{ad} \ + HCOO_{ad} \tag{6}$$

$$H_{ad} \qquad = H^+ + e^- \tag{4}$$

$$HCOO_{ad} \ = \ CO_2 + H^+ + e^- \tag{7}$$

has been generally accepted in the literature (17). The present results indicate that such a mechanism cannot continue at potentials negative to 0.300 V in H_2SO_4 at Pt electrodes

*For example, after potentiostating the Pt electrode in CO_2-saturated solution at -0.120 V, the oxidation plateau of the X region was still present at about 0.950 V on the anodic charging curve when the pulse current was 2.33 A/cm^2.

at 25°C. After sufficient interaction of H_{ad} and CO_2, the HCOOH dissociation could not proceed on a major fraction of the electrode surface because of the blocking effect of CO_2.

A decrease in current with time is generally found for the potentiostated oxidation of organic compounds. Recently it has been suggested that this might be due to "reduced CO_2." However, this work shows that under steady-state conditions CO_2 cannot block H_{ad} oxidation at or above 0.300 V. Hence, a poisoning effect due to this at potentials above 0.300 V is impossible. The present results also imply that the complete oxidation of organic compounds on Pt at potentials below 0.300 V to obtain higher cell voltages in electrochemical energy converters may not be feasible.

CONCLUSIONS

1. CO_2 in solution, or possibly HCO_3^-, interacts strongly on Pt to affect H adsorption. The rate of interaction is relatively slow; about 15 min are required to attain limiting conditions.

2. The interaction is apparently not simple physical adsorption of CO_2 on the metal substrate, and a reduced CO_2 surface compound or a soluble species that is stable in solution are not formed. The H_{ad} blocked by CO_2 interaction is stable on the surface and irreversibly sorbed.

3. The oxidizable species is not CO.

4. Limiting H_{ad} blocked by CO_2 or HCO_3^- is ≈ 260 $\mu coul/cm^2$. This H_{ad} is stable at potentials negative to 0.3 V. When potentiostated at 0.300 V, it is completely oxidized.

5. CO_2 or HCO_3^- inhibits the H_2-evolution reaction on Pt.

6. Coulometric measurements strongly indicate that active or weakly bound H is present on the electrode below about 0.150 V, but not above this potential.

7. It is tentatively suggested that HCOOH dissociates to H_{ad} and CO_2, and that CO_2 or HCO_3^- interacts on Pt to retard oxidation of HCOOH.

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The effect of CO_2 on the oxidation of H atoms chemisorbed on a Pt electrode is examined with potentiostatic and transient galvanostatic techniques. The results indicate that CO_2 is not reduced, but that H_{ad} oxidation is inhibited by CO_2, or possibly HCO_3^-. Under these conditions the inhibited or blocked H_{ad} is stable at potentials negative to 0.300 V (vs N.H.E.). Dissociation of HCOOH to H_{ad} and CO_2 may inhibit the further oxidation of HCOOH by a similar blocking mechanism.

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